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Superior Mesoporosity of Lipid Free Spent Coffee Grounds Residues

Thomas I.J. Dugmore*, Zhiren Chen, Stella Foster, Charlie Peagram and Avtar S. Matharu*

Abstract: As part of the biorefinery concept for spent coffee grounds (SCG), production of activated carbon (AC) was investigated from the degreased coffee grounds (DCG) left behind after oil extraction (primarily for biodiesel). The oils were extracted via conventional solvent extraction with GC/GC-MS confirming the oil was comparable to oils produced industrially. More significantly, analysis showed the DCG AC to have a 4-fold increase in mesoporosity than the SCG AC with mesopore volumes of 0.6 and 0.15 cm^3 g^{-1} respectively.

Adsorption trials showed a ten-fold increase in capacity for Au(III) from 8.7 to 88.6 mg/g with subsequent experiments confirming that DCG AC displayed standard behavior for mesoporous materials of increasing adsorption capacity with decreasing pH. This raises the potential for valorization of SCG into a functional material for water remediation without the need for templating agents or expansion pre-treatments with the added bonus of an additional material being produced simultaneously.

Introduction

At present, coffee is one of the most popular beverages on Earth, of which consumption continues to increase. According to the International Coffee Organization, 9 billion kg of coffee beans are produced per year,[1] whilst the Food and Agricultural Organization of the United Nations estimates that this figure is increasing by 2.5 percent annually.[2] The production of coffee inevitably leaves behind the water-insoluble residues, known as spent coffee grounds (SCG), as waste; approximately, 6 billion kg (6,000,000 tons) of wet SCG are produced per year as unavoidable food supply chain waste (UFSCW). [3] UFSCW is an increasing problem worldwide as its generation is inevitable throughout the production chain from farm to fork through the discarding of inedible portions; yet with an increasing population comes an increased demand for food. Combined with avoidable food waste, such as inefficiencies in production and wasteful practices in homes and retail, it has been estimated that if food waste were a country, it would be the third largest greenhouse gas emitter behind China and the USA.[4] With more food needed for a growing population, the amount of UFSCW is inevitably set to increase.

The usual disposal methods for UFSCW are largely landfill, but also include incineration for energy, compositing, animal feed and, more recently, anaerobic digestion. These are not without issue though as landfilling and anaerobic digestion generate methane,[5] which is a potent greenhouse gas,[6] although with the latter it is mainly recovered for energy. As landfill space is also reducing, there are increasing incentives to reduce the amount of food waste generated. This was made a specific target under goal number 12 in the United Nations release of the 17 Sustainable Development Goals highlighted as Target 12.3: 'By 2030, to halve per capita global food waste at the retail and consumer levels and reduce food losses along production and supply chains, including post-harvest losses'.[7]

With increasing pressure to find alternatives to petroleum for fuels and materials, and the 'food vs fuel' debate[8] arising from the use of food grade biomass for this purpose, UFSCW has begun receiving a large amount of research interest as a means of addressing both these issues.[9] The biorefinery concept is also one that is becoming increasingly popular – the idea of taking biomass as a feedstock and processing it into several different products and materials as opposed to a single target product.[10]

At a basic level, one of the common uses of SCG is simply as a fuel for biomass burning; however the high nitrogen content from caffeine and theobromines present is a drawback due to subsequent NO_x emissions. This is also an issue when sending them for anaerobic digestion as the nitrogen is first anaerobically reduced to ammonia, which is then converted to NO_x upon combustion. The theobromine content also makes them poisonous to ruminants, thereby significantly removing animal feed as a viable option too.

Another potential use of SCG is the production of Activated Carbons (ACs). Published results to date report that ACs derived from SCG have surface areas between 645-1380 m^2/g,[11] which is comparable to ACs made by other agriculture wastes, which possess surface areas between 250-2410 m^2/g.[12] Whilst ACs are widely used commercially as microporous adsorbents, they are limited in higher technological or value applications due their low selectivity and poor recyclability. Huang et al conducted a review of the literature on activated carbons and their more advanced composites in development and showed that modification of the materials or or carbonization processes were necessary to achieve higher surface areas, porosity and specific active sites for binding.[13] There is also, therefore, a growing interest in the area of mesoporous materials (pores with a diameter of 2-50 nm)[14] due to the increased surface area and pore volume they confer. This allows a much higher loading capacity over microporous materials, making it a more effective sorbent for large species such as heavy metals or dyes.[15] Being larger, mesopores are less prone to being clogged by the adsorbate than their microporous counterparts, allowing both regeneration of the material, and recovery of the adsorbate for re-use.[16] However the process for creating mesoporous materials typically requires the use and synthesis of templating agents to form the network around, which must be subsequently removed and disposed of, generating copious amounts of waste.[15a, 17]

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Supporting information for this article is given via a link at the end of the document.

Other methods, such as Starbon® Technologies have removed the need for templating agents by using the natural polymer matrix of carbohydrates, such as starch, alginic acid and pectin, as the backbone for the material.[18] The porous network is generated by superheating the polymer in water, forcing the matrix to expand. However, this method is not without its drawbacks – notably the need to remove the water from the network either via solvent exchange or freeze drying prior to pyrolysis, thereby also generating copious amounts of waste (albeit recoverable waste) or requiring relatively energy intensive processes. SCGs have been trialed for use in producing mesoporous materials by direct activation with zinc chloride and potassium hydroxide to avoid templating or solvent exchange.[19] However, whilst a mesoporous network was successfully achieved, the highest mesopore volume reported was only 0.34 $cm^3\ g^{-1}$ which is lower than the typical ranges of 0.5-0.7 $cm^3\ g^{-1}$ typically reported for commercially available materials and the higher end reported values of 1.0-1.2 $cm^3\ g^{-1}$.[18a, 18b, 20] Additionally, the material still exhibited a large degree of microporosity with micropores making up 69-77% of the total pore volume.

Whilst SCG have attracted a large amount of interest for the purpose of waste valorization, as has the biorefinery concept for waste biomass as a whole, it is somewhat surprising that most papers have concentrated only on single applications of SCG meaning that some portions are often left wasted or underutilized. For example, when the lipids are extracted for biodiesel or cosmetics, the residues are left behind after being filtered off which still account for >80% by mass of the total SCG. Similarly, when pyrolizing to produce activated carbon, all volatile and flammable material is lost to either evaporation or decomposition which, at the temperatures typically required for pyrolysis, would be expected to include the lipid portion.

Herein, the potential of producing both products from a single batch of SCG to increase the valorization efficiency is reported. The oil was extracted from one portion of SCG and analyzed via GC-MS to confirm that the profile was comparable to other coffee oils used to make biodiesel. Heptane was used instead of hexane in this study as it shows similar characteristics on lipids extraction[21] and is considered a greener solvent compared to the undesirable hexane.[22]

Activated Carbon was then produced from both normal and degreased SCG (DCG) using $ZnCl_2$, according to methodologies previously reported.[11b-d, 23] Their structural properties were compared, as were their abilities to adsorb Cr(VI) and Au(III) against each other and a commercially available NORIT sample. These metals were chosen as hexavalent chromium is a serious problematic pollutant for the water industry, being produced from many sources including ore refineries, leather tanneries, electroplating and cement production.[24] Gold meanwhile is a precious metal used primarily in jewelry and catalysis, yet with diminishing reserves and very low recycling rate at present. Both are currently under supply chain threat;[25] gold in particular is listed as being under serious risk of all known reserves being depleted in less than 50 years. Removal and recovery of them from effluent streams therefore also offers a potential means of addressing both issues. Thus, this is the first reported study of the simultaneous production of both biodiesel and activated carbon from lipid-free spent coffee grounds and its potential for usage in metal adsorption/recovery from aqueous solutions.

Results and Discussion

AC adsorption capacity

The Au(III) and Cr(VI) concentration reduce rates from the adsorption experiments are showed by Tables 1 and 2 respectively, at pH7 and standard conditions. It can be clearly seen from these tables that the DCG AC gave superior adsorption performance compared to the standard SCG AC for Au with 91.5% of Au(III) adsorbed by the DCG AC after 40 minutes stirring compared to just 8.5% with SCG AC under the same conditions – over a 10-fold improvement.

Table 1. Concentration of Au(III) [g dm^{-3}] in solution with different ACs

Time/min	DCG AC	SCG AC	NORIT®
0	0.20	0.20	0.21
10	0.05	0.19	0.10
20	0.02	0.18	0.10
30	0.02	0.18	0.09
40	0.02	0.18	0.09

Table 2. Concentration of [Cr(VI)] /g dm^{-3} in solution with different ACs

Time/min	DCG AC	SCG AC	NORIT®
0	2.50	2.50	2.30
10	2.27	2.29	2.18
20	2.26	2.25	2.14
30	2.26	2.22	2.14
40	2.26	2.24	2.12

Comparable performance was noted on Cr for both coffee derived ACs however, but both displayed superior adsorption compared to the NORIT® standard AC. The mass adsorbed at each time (q_t) was calculated according to equation 1 and the equilibrium adsorption (q_e) according to equation 2, where C_0 and C_e are the initial and equilibrium concentrations respectively C_t, the concentration at time t, V is the volume of solution and w is the mass of the adsorbent. The data was then modelled using pseudo-first order kinetics according to the methodology set out by Aljeboree et al.[26] The results are shown in Figures 1 and 2 for Au and Cr respectively from which it can be seen that the adsorption capacity obtained from the experiments fits well with the theoretical plot.

Equation 1 $q_t = \frac{(C_0 - C_t) \times V}{w}$

Equation 2 $q_e = \frac{(C_0 - C_e) \times V}{w}$

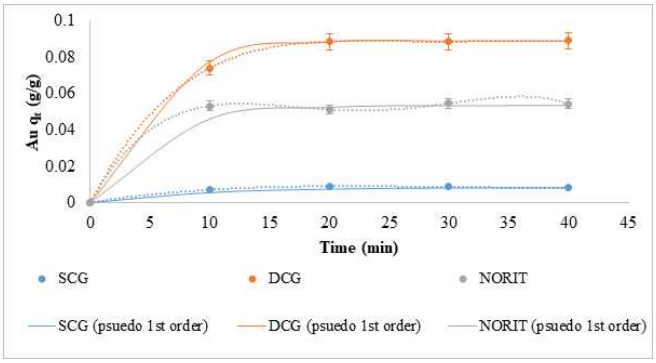

Figure 1. The amount of gold adsorbed per g of AC.

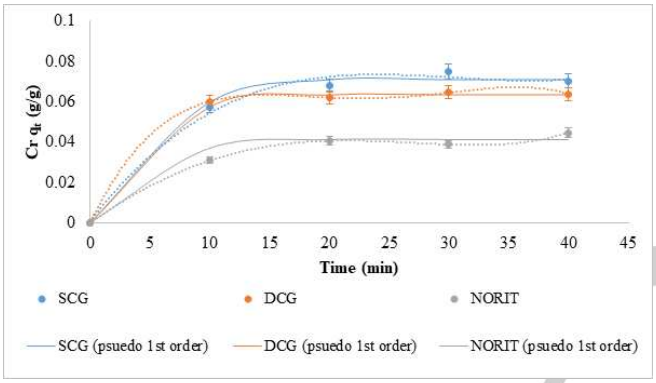

Figure 2. The amount of chromium adsorbed per g of AC.

Effect of pH

Following on from the initial comparative adsorption experiments, adsorption with varying pH (regulated by HCl and NaOH) on the DCG AC was carried out with the results shown in Figure 3. The figure shows that the DCG AC exhibits the expected trends displayed by mesoporous materials of increasing adsorption capacity with decreasing pH, with adsorption stopping completely at strong alkaline conditions suggesting the possibility for desorption and therefore recovery of these metals by altering pH. The q_e was also measured against the ionic strength of the solution, however this did not show any notable trends. The resulting figures are provided in the Supplementary Information.

AC properties

The porosity data shown in for both ACs during pyrolysis are shown in Table 3, along with the data for the commercial NORIT sample which clearly shows that the DCG AC has a significant increase (4x) of mesoporosity compared to the SCG AC. This also represents nearly double the previously highest reported value from SCG of 0.34 $cm^3\ g^{-1}$ and near complete conversion to mesoporosity with mesopores making up 96% of the porous network compared to just 27% previously reported.[19]

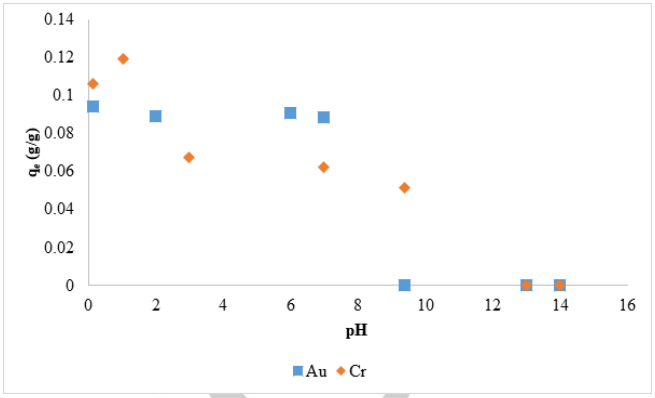

Figure 3. The adsorption of Au and Cr onto DCG at varying pH.

Table 3. Porosimetery data for the ACs.

AC variety	SCG	DCG	NORIT®
BET Surface Area [$m^2\ g^{-1}$]	878.81	811.53	525
Langmuir Surface area [$m^2\ g^{-1}$]	1168.96	1118.00	730
t-Plot micropore area [$m^2\ g^{-1}$]	603.47	71.24	497
Pore Volume [$cm^3\ g^{-1}$]	0.43	0.62	0.28
Micropore Volume [$cm^3\ g^{-1}$]	0.28	0.023	0.24
Mesopore Volume [$cm^3\ g^{-1}$]	0.15	0.60	0.04
Mesopore:Micropore ratio	0.54	26.09	0.17
Mesoporosity [%]	34.88	96.77	14.29

There are a couple of potential explanations for this observation. The first is that the lipids were not completely vaporized during the process. The temperature of vaporization of lipids is typically round 400 °C, depending on the nature of the fatty acid chains. The carbonization temperature was set to 600 °C, which therefore should be high enough to vaporize the material, although this may require more time than was given due to the nature of the mixture.

Alternatively, there is the possibility of the polyunsaturated fats polymerizing to form heavier, non-volatile resins. Hence, the non-vaporized lipids could also block the vaporization route of other substances. When carbonaceous material is heated to high temperatures, most of the heteroatoms (chiefly nitrogen and oxygen) and hydrogen are removed in a gaseous form,[27] creating interstices within the structure. However, these interstices can be blocked by tar or resin formation. By extracting the lipids prior to carbonization, this could possibly provide a more porous material, but could also aid the formation or enlarging of pores by allowing easier decomposition of the surface structure. The chemical activation method can inhibit tar formation, though there is still uncertainty as to whether the inhibition mechanism is chemical (interfering with the reaction) or physical (blocking the pores where tar would otherwise be

formed) or a combination of both.[12a, 27-28] Either way, $ZnCl_2$ is water-soluble and may be washed out to afford a porous structure with higher adsorption capacity.

The porosimetry data in table 3 appears to support this – the DCG shows in increase of ca. 50% in pore volume compared to its SCG counterpart and, crucially, an increase of ca. 400% in mesopore volume.

The porosimetry and adsorption data is also supported by TEM) images of the material, summarized in figures 4-7 (all individual TEM images available in supplementary information). Overall the images appear to show the grounds initially appearing to be very granular structures, before becoming more open upon lipid extraction and even more so following pyrolysis – a feature not observed when the lipids were not extracted.

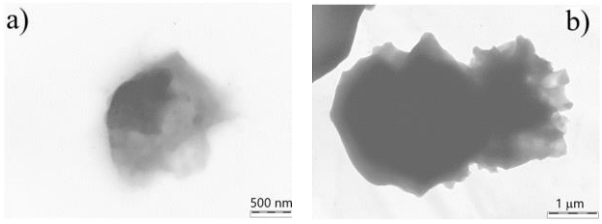

Figure 4. TEM images of the SCG (a) and DCG (b) prior to carbonisation.

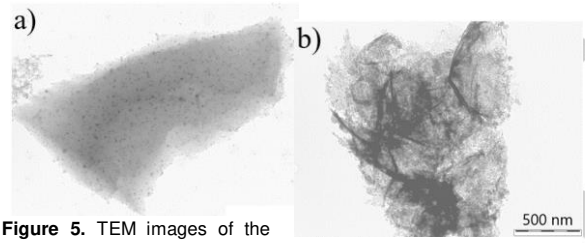

Figure 5. TEM images of the SCG AC (a) and DCG ACG (b).

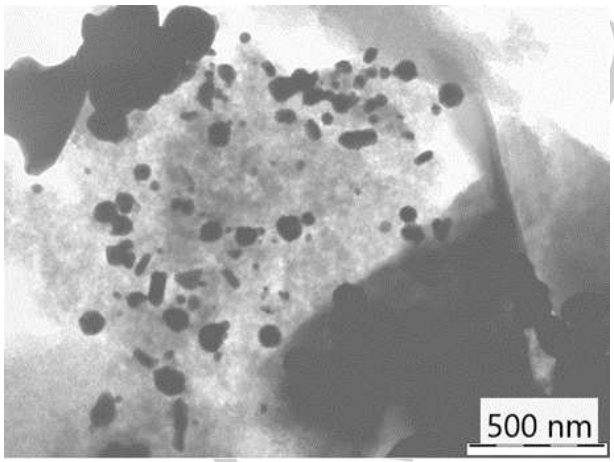

Figure 6. TEM image of the DCG AC after adsorbing gold.

Figures 7 and 8 show the XPS images obtained for the samples and ACs respectively (3 scans were run on each sample – all are available in supplementary information). These show that whilst the oxygen and nitrogen peaks diminish significantly in intensity relative to the carbon peaks during carbonization, they do not disappear completely suggesting that full carbonization has not yet been achieved. Additionally, the AC scans clearly show the appearance of zinc and chlorine peaks indicating that complete removal of the zinc has not been achieved. They appear to show a reduction in the intensity of the carbonyl peak upon lipid extraction, which is consistent with the loss of the fatty acids/esters, with only a slight shoulder in the C-O region remaining, which appears to remain upon pyrolysis. At present, this is attributed to the hydroxyl groups from the carbohydrate macromolecules (primarily cellulose) which have not completely been removed through the pyrolysis step. The carbon region is zoomed in on figure 9 for clarity.

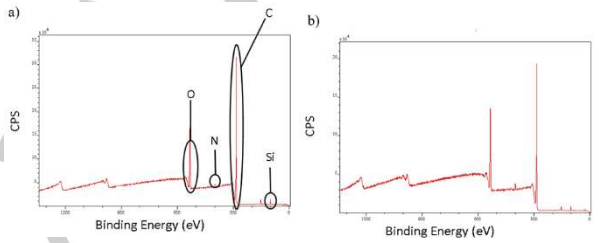

Figure 7. XPS scans of the initial SCG (a) and DCG (b).

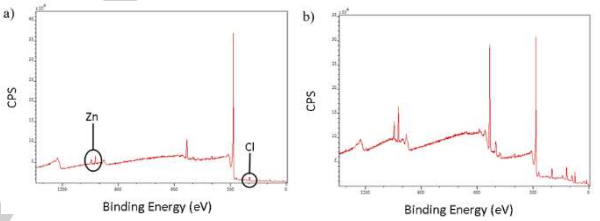

Figure 8. XPS scans of the SCG AC (a) and DCG AC (b).

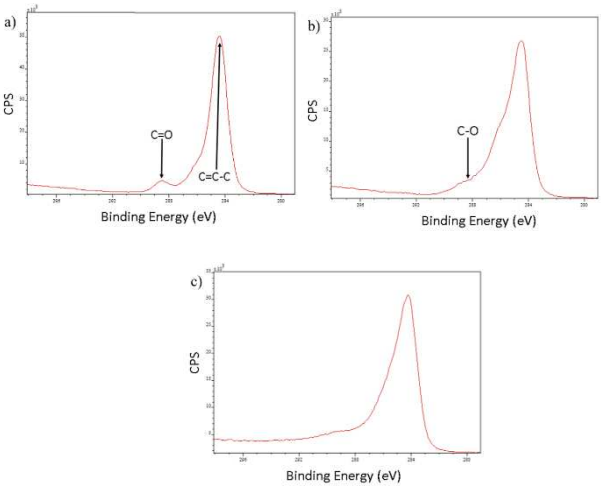

Figure 9. The carbon scan sections of the XPS of a) the SCG, b) DCG and c) DCG AC

Figure 10 shows the solid-state NMR spectra of the SCG samples and resulting ACs which support the XPS spectra showing a significant loss of C=O and C-O signals upon carbonization leaving signals, suggesting an aromatic or graphitic surface to the ACs. For further characterization of the carbon surface functionalities (CSF) Boehm titrations were carried out. The results are shown in Table 4 with the error bars representing the standard deviations from the mean of the titration results, with the exception of the phenolic groups, which are calculated according to equation 3.

Equation 3

$$Phenolic\ CSF = Total\ CSF - Carboxylic\ CSF - Lactonic\ CSF$$

Table 4. The Boehm titration results.

Number of Carbon Surface Functionalities [mmol g^{-1}]				
AC type	Total Acid	Carboxylic	Lactonic	Phenolic
DCG	4.24 ± 1.63	4.83 ± 0.47	0.15 ± 0.3	-0.74 ± 1.6
SCG	3.46 ± 1.23	4.34 ± 0.32	0.14 ± 0.4	-1.12 ± 1.53

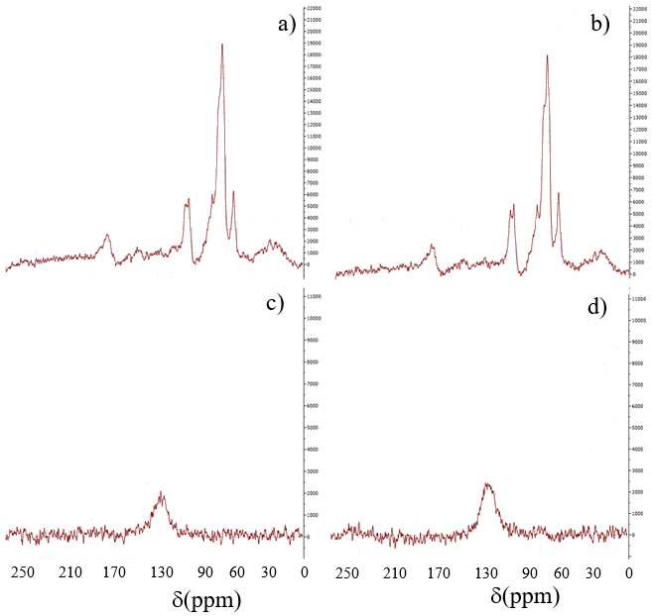

Figure 10. The solid state NMR spectra of SCG (a), and DCG (b), SCG AC (c) and DCG AC (d).

From this, it can be seen that the material still retains some very weak acidic character, which appears to be primarily carboxylic in nature; nearly all lactonic and phenolic character has disappeared. The negative reading for phenolic character stems from the subtractions in equation 3 based upon the standard error for the previous titrations and is therefore likely to be zero – which matches observations about the surface properties on other mesoporous carbonaceous materials.[18b]

The graphitic nature of the material, coupled with the retention of slight acidic character also helps explain why both Au and Cr ions can be adsorbed despite being very different in character (+ve and –ve charge respectively). Due to the negative charge on the Cr(VI) ion, the good adsorption in acidic media is to be expected as the AC surface is more heavily protonated and therefore carrying a relative positive charge. Similarly, the alkaline conditions deprotonate the surface acidic groups rendering it with an overall negative charge.[29] As Au is positively charged however, conventional adsorption models onto AC would suggest the opposite trend. However, studies carried out on platinum group metal adsorption onto other mesoporous carbons in acidic media have suggested that the graphitic surface acts as a reducing agent for the metal ions in question prior to adsorption.[30] As the XPS in figure 9 also shows mainly graphitic character, it is likely the mechanism is the same here. However, this mechanism is far harder to occur in microporous materials due to the small pore size (<2 nm) making it harder to accommodate the ions. This is also supported by the observation that the increase in mesopore volume notably increases the adsorption capacity for Au(III) but does not have as notable an effect on Cr(VI) adsorption. To summarize, the mechanism of Cr(VI) adsorption is likely to be physi-sorption, whereas the mechanism for Au adsorption may be due to chemisorption.

ICP analysis of all of the ACs were also carried out, as well as on the DCG after treatment with $AuCl_3$ and $K_2Cr_2O_7$ at pH 7. This showed that there were only trace levels of all the metals present initially and that the concentration of Au and Cr in the AC increased over 50,000x and 30,000x respectively, over the 40 min period (results shown in Table 5). This is consistent with the observation of higher q_e values observed in the UV/Vis analysis of the solution and confirms that the ACs are indeed removing metals from the solutions, as opposed to merely changing the UV/Vis absorbance by chemical reactions, e.g. ligand exchange or changing the oxidation states of the metals.

Table 5. ICP data in the ACs

Metal [ppm]	SCG AC	DCG AC	Cr-DCG AC	Au-DCG AC	NORIT®
Au	0.61	0.18	1.59	58736.8	0
Cr	0.68	1.45	36452.70	19.77	24.45

The UK regulations require the maximum concentrations of Cr^{3+} in tap water to be less than 50 μg L^{-1}.[31] Current EU regulations for wastewater allow effluent to be disposed of to the water course below 1,000 mg L^{-1} for Cr(VI).[32] The above discussion showed that the DCG AC can handle 20,000 mg L^{-1} solutions of this metal at a capacity of 120 mg g-1, which is superior to most common Cr adsorbants,[33] thereby demonstrating their potential to be used for effluent treatment, potentially for recycling or recovery and potentially others too.[34] Due to the remaining zinc in the material, there is potentially scope to increase the observed adsorption capacities by improving the efficiency of the

washing stage. Fortunately, the behaviour of the zinc and the characterisation of the AC indicate very similar properties to other bio-mass derived mesoporous materials,[35] meaning data obtained on these materials so far could provide a useful insight into means to achieve increased efficiency in future work. As a summary, a comparison of the adsorption results compared with other materials is shown in Table 6

Table 6 – The q_e of Au(III) and Cr(VI) on various carbonaceous materials

Material	Au(III)q_e (g/g)	Cr(VI) q_e (g/g)	Ref
SCG AC	0.0088	0.075	This work
DCG AC	0.0943	0.1195	This work
Coconut Tree AC		0.0034	Selvi et al[29a]
Fox nut AC		0.075	Kumar et al[29b]
Olive Bagasse AC		0.126	Demiral et al[29c]
Porous Graphitic Carbon	0.0075		Sun et al[36]
Apricot Stone AC	0.0302		Soleimani et al[37]
HSAS carbon	0.00506		Soleimani et al[37]

Conclusions

Overall, this work has demonstrated the potential for SCG to be valorized into two different products – biodiesel and AC – from a single feedstock in a biorefinery concept. Additionally, the work has demonstrated that the resulting AC has superior mesoporosity to ACs produced directly from SCG in the same manner and represent a clear improvement on previous attempts to make mesoporous carbon from SCG.

Future work will therefore examine desorption and recovery of the adsorbents, as well as the possibility to adsorb and recover other metals or molecules of interest currently consigned to waste streams and lost.

Experimental Section

Materials

SCG (*Arabica* variety) was supplied by the Library Café (Costa Coffee) at The University of York, UK. To avoid mold growth, SCG was dried in an oven at 105 °C until constant weight was achieved before being stored. Methanol (HiPerSolv CHROMANORM), ethanol (absolute, AnalaR NORMAPUR) and heptane (HPLC grade) were purchased from VWR chemicals. KOH, NaOH, HCl (both Analytical Reagent Grade), Na_2CO_3 (Laboratory Reagent Grade) were all purchased from Fisher scientific. $AuCl_3$ and potassium dichromate were both purchased from Sigma Aldrich. $NaHCO_3$ (99.5% for biochemistry) was purchased from Acros Organics and $ZnCl_2$ (anhydrous, 98%) was purchased from Alfa Aesar. NORIT® activated carbon was purchased from Syngenta. Nitrogen was produced by boiling off a liquid nitrogen tanks supplied by BOC. No additional purification was carried out prior to usage for any of the chemicals.

Lipid Extraction

Dry SCG (30 g) was heated under reflux for one hour in heptane (60 ml) and thereafter, the resultant slurry was filtered under vacuum. The solvent was then removed under rotary evaporation, until constant mass was achieved, affording a dark brown oil.

Production and testing of AC

10 g each of both SCG and degreased SCG (DCG) were mixed with 20 g zinc chloride in a 2:1 ratio. Deionized water was added until the mixture formed a mobile slurry, which was then stirred for 10 minutes. The slurry was dried in an oven at 105 °C for 24 h and the resultant dry mixture was ground in to a fine powder prior to carbonization in a furnace oven under a nitrogen flow of 100 cm^3 min^{-1}. The furnace temperature was increased to 600 °C at a ramp rate of 10°C min^{-1} and then held for 30 minutes giving a total time of 90 minutes. The cooled carbonized crude product was washed with 0.5 mol dm^{-3} HCl (3×30ml) followed by deionized water (3×30 ml) to remove $ZnCl_2$ and other impurities and dried in an oven (105 °C) until constant weight was achieved to afford the activated carbon.

The metal ion adsorption abilities of the SCG AC and DCG AC were tested by using their chloride (Au) and potassium (Cr) salts in deionized water. λ_{max} was measured for each and calibrated to the selected wavelengths: 287.6 nm (Au(III)) and 377.0 nm (Cr(VI)) on a Jenway 6705 UV/Vis-Spectrophotometer.

The adsorption ability was tested by mixing 0.2 g of the ACs with the appropriate metal ion solution with concentration and pH being the variables altered. HCl and NaOH were used to modify pH. The mixtures were stirred, 5 mL aliquots were taken at intervals, filtered under gravity and the subsequent metal concentration of each sample was measured via UV-vis spectroscopy. For control, these were compared against commercial NORIT® activated carbon.

Characterization of the ACs was carried out via porosimetry, TEM, XPS, solid state ^{13}C NMR, Boehm titration and IPS-OES.

Analytical Methods

Porosimetry was carried out on a Micrometrics ASAP 2020 porosimiter. 0.1g of sample was measured accurately into a sample tube, which was then degassed under vacuum for 24 hours at room temperature. Nitrogen was then introduced to the tube until uniform partial pressure is obtained and the resulting surface area and porosity calculated from the volume of nitrogen adsorbed.

Boehm titrations were carried out on the material according to the standardized method set out by Goertzen et al using both manual and automated titration systems. [38] Stock solutions of Hydrochloric acid,

sodium carbonate, sodium hydrogen carbonate and sodium hydroxide (all 0.05M) were made up and degassed overnight by bubbling N_2 through them. 0.1g of sample was accurately measured out into 50 mL of each solution, shaken overnight and filtered to remove the carbon. For the alkaline solutions, 10 mL aliquots of the NaOH and $NaHCO_3$ solutions were acidified with 20 mL of the HCL solution, for the Na_2CO_3 solution, 30 mL of HCl was used. The solutions were then back-titrated against the NaOH solution in triplicate on a Metrohm 907 Titrando auto-titrator with the pH being monitored by pH probe and once manually using phenolphthalein as a visual indicator. The HCl solutions were titrated directly against NaOH solution using the same methods.

^{13}C-CP-MAS NMR spectra was acquired using a Bruker AVIII HD 400 MHz spectrometer. Samples were spun at 12 kHz for 15000 scans and referenced to external adamantine.

TEM was carried out via the Technology Facility analytical services at the University of York Biology department. XPS and ICP-OES were carried out externally at Newcastle University NEXUS service and Yara Analytical services respectively.

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Keywords: Spent Coffee Grounds, Mesoporous Carbon, Environmental Remediation, Waste Mitigation, Metal capture

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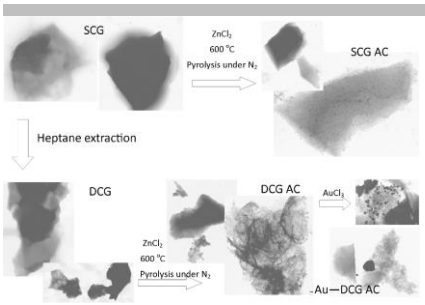

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